PATENT ABSTRACTS OF JAPAN

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(71)Applicant : NGK INSULATORS LTD
(72)Inventor : BOUGAKI TOMOHIRO
ONO TADASHI
NAKAGAWA TOSHIHIKO

(54) POLARIZABLE ELECTRODE FOR ELECTRIC DOUBLE-LAYER CAPACITOR

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a polarizable electrode for an electric double-layer capaci tor capable of reducing a long term deterioration of a performance of the capaci tor and an energy loss due to a selfdischarge.
SOLUTION: The polarizable electrode for the electric double-layer capacitor comprises a carbon fine powder, a conductive assistance and a binder. A tensile strength of the electrode is 0.13 MPa or more.

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[Claim(s)]

[Claim 1] The polarizable electrode for electric double layer capacitors characterized by being the polarizable electrode for electric double layer capacitors which consists of carbon fines, a conductive assistant, and a binder, and the tensile strength of the aforementioned polarizable electrode being 0.13 or more MPas.

[Claim 2] The polarizable electrode for electric double layer capacitors according to claim 1 whose degraining particle weight of the carbon particle to the inside of the electrolytic solution is two or less 1.0 mg/cm.

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the polarizable electrode for electric double layer capacitors.

[0002]

[Description of the Prior Art] Now, in the field of various kinds [electric double layer capacitor / configuration / of the shape of the sheet], the use development is performed actively. Especially, drastic curtailment of the amount of the fossil fuel used by the automobile is called for from the environmental problem and the resources problem, and the so-called high Brit car which can reduce the amount of the fossil fuel used by the combined use with a fossil fuel and the electrical and electric equipment is capturing the spotlight as one of the policies of this curtailment. In this field, much more high-power-density-ization of a high-power-density type electric double layer capacitor is called for. On the other hand, the use as the so-called backup power supply of a personal computer or various electrical machinery and apparatus is also increasing. in this field, although the high-energy density type electric double layer capacitor is used, much more quantity energy-density-ization is called for

[0003] For this reason, as for the polarizable electrode used for an electric double layer capacitor, it is indispensable to raise the density of the carbon fines in a polarizable electrode.

[0004] However, if the polarizable electrode used now infiltrates the electrolytic solution, in order for the carbon particle in a polarizable electrode to tend to degrain it, it had the problem that the performance of an electric double layer capacitor will deteriorate. Moreover, since the

above-mentioned polarizable electrode had many carbon particles which float in the electrolytic solution, it had the trouble that self-discharge became large and the energy loss of an electric double layer capacitor became large.

[0005]

[Problem(s) to be Solved by the Invention] the place which this invention is made in view of the technical problem which such conventional technology has, and is made into the purpose offers the polarizable electrode for electric double layer capacitors which can reduce the energy loss by the long-term performance degradation and long-term self-discharge which are an electric double layer capacitor by suppressing degraining of the carbon particle in the polarizable electrode at the time of electrolytic-solution sinking in

[0006]

[Means for Solving the Problem] That is, according to this invention, it is the polarizable electrode for electric double layer capacitors which consists of carbon fines, a conductive assistant, and a binder, and the polarizable electrode for electric double layer capacitors to which tensile strength of the aforementioned polarizable electrode is characterized by being 0.13 or more MPas is offered. At this time, it is desirable that the degraining particle weight of the carbon particle to the inside of the electrolytic solution is two or less 1.0 mg/cm in this invention.

[0007]

[Embodiments of the Invention] The polarizable electrode of this invention is a polarizable electrode for electric double layer capacitors which consists of carbon fines, a conductive assistant, and a binder, and the tensile strength of a polarizable electrode is 0.13 or more MPas. Thereby, since degraining of the carbon particle in the polarizable electrode at the time of electrolytic-solution sinking in can be suppressed, the energy loss by the long-term performance degradation and long-term self-discharge of an electric double layer capacitor can be reduced.

[0008] As for the polarizable electrode of this invention, at this time, it is desirable that the degraining particle weight of the carbon particle to the inside of the electrolytic solution is two or less 1.0 mg/cm. This is because the long-term performance of an electric double layer capacitor deteriorates since the carbon particle which floats in the electrolytic solution increases and the rate of self-discharge at the time of real use of an electric double layer capacitor becomes large, when the degraining particle weight of the above-mentioned carbon particle exceeds 1.0 mg/cm2.

[0009] Moreover, since the polarizable electrode of this invention can make the rate of self-discharge of an electric double layer capacitor 10% or less, it can reduce the energy loss of an electric double layer capacitor.

[0010] In addition, the carbon fines used by this invention adsorb the anion and cation which exist in the electrolytic solution, form an electric double layer, and act for accumulation of

electricity. Moreover, the conductive assistant used by this invention raises the electrical conductivity of carbon fines and carbon fines, and a charge collector. Therefore, the mixed rate of carbon fines plays an important role in the improvement in an energy density of per unit area in a polarizable electrode, and the mixed rate of a conductive assistant influences internal resistance, and contributes to the improvement in power density. For this reason, according to the purpose of using a polarizable electrode, you should adjust the mixed rate of a conductive assistant. For example, as an object [like / for power storage] for high-energy densities, the mixed rate of a conductive assistant is 3 - 10 weight section to the carbon fines 100 weight section, and it is desirable that it is 8 - 20 weight section to the carbon fines 100 weight section as an object / like / for electric vehicles] for high power density.

[0011] The mixture which the kneading object used by this invention turns into from the conductive assistant 3 - 20 weight sections to the carbon fines 100 weight section is used suitably. This is because internal resistance becomes large and power density decreases, when conductive assistants are under 3 weight sections. On the other hand, when a conductive assistant exceeds 20 weight sections, in order that the mixed rate of the carbon fines which internal resistance hardly reduces and are conversely occupied in a unit volume may decrease, an energy density will fall.

[0012] As for the binder used by this invention, it is desirable that it is a fluororesin, for example, the thing of a publication can use it for JP,7-44127,B suitably. That is, a polytetrafluoroethylene (PTFE) and ethylene-tetrafluoroethylene copolymer, an ethylene-chlorotrifluoroethylene, a fluoride vinylidene copolymer, a tetrafluoroethylene-perphloro alkylene vinyl ether copolymer, etc. are mentioned. Especially, a tetrafluoroethylene is suitably used from a chemically stable thing.

[0013] As for the mixed rate of the above-mentioned fluororesin, at this time, it is desirable that it is 3 - 15 weight section (preferably 5 - 10 weight section) to the carbon fines 100 weight section. This is because tensile strength cannot obtain the sheet-like Plastic solid of 0.13 or more MPas when fluororesins are under 3 weight sections. It is because internal resistance not only increases, but the rate for which carbon fines account to per unit area relatively falls on the other hand when a fluororesin exceeds 15 weight sections.

[0014] Next, the manufacture method of the polarizable electrode of this invention is explained in detail based on a drawing. Drawing 1 is a flow chart which shows an example of the manufacture method of the polarizable electrode of this invention. As shown in drawing 1 , it mixes so that the binder which consists of the end of a carbon powder the conductive assistant 3 - 20 weight sections were added and adjusted to the carbon fines 100 weight section of the specified quantity, and a fluororesin first may distribute uniformly (raw material mixture process). In order to suppress the fibrosis of a fluororesin at this time, it is desirable to mix below with the transition temperature (in the case of PTFE 19 degrees C or less) of a fluororesin.

[0015] The mixture obtained at the raw material mixture process is fully kneaded, applying shearing force heating at 20-120 degrees C using the kneading equipment shown in drawing 2 (kneading process). The fluororesin which is a binder becomes microfilament-like by this, it binds mutually, and the kneading object with which appearance volume with small bulk density consists of a 0.01-10cm wafer group which is about three is obtained. In addition, even if kneading temperature is high, about 120 degrees C of it are [that a fluororesin should just be the temperature (for example, 50 degrees C) which shows sufficient fluidity] enough. Moreover, the shearing force and the mixing time to add are enough if each material is the conditions kneaded fully and uniformly. Furthermore, at a kneading process, you may add a fluid lubrication agent for fibrosis promotion of a binder.

[0016] The kneading object obtained at the kneading process is fabricated by the sheet-like Plastic solid of predetermined thickness (for example, 0.3mm) with the roll-press equipment shown in drawing 3 (sheet forming cycle). At this time, by binding partially the fluororesins which became microfilament-like, intensity of the above-mentioned sheet-like Plastic solid increases more, and it can fix carbon fines more firmly.

[0017] Although it can be used as a polarizable electrode even if it remains as it is, the sheet-like Plastic solid obtained by the sheet forming cycle serves as a sheet for polarizable electrodes for capacitors by rolling out until it becomes thickness (for example, 0.2mm) predetermined with the rolling equipment (rolling roller) shown in drawing 4 , when controlling thickness with a more sufficient precision, or when the further improvement in density is required. The polarizable electrode for capacitors made into the purpose can be obtained by cutting out this sheet in a desired size at the last.

[0018]

[Example] Hereafter, although an example explains this invention concretely, this invention is not restricted to these examples. In addition, the sheet for polarizable electrodes and electric double layer capacitor which were obtained in each example evaluated the performance by the method shown below.

[0019] (Measuring method of tensile strength) JIS It measured according to K6301.

[0020] (Measuring method of a degraining particle weight) The sheet for polarizable electrodes was pierced to phi19mm to punch etc., was dried enough, and the initial mass W1 was found. Next, after making this sheet immersed into an acetonitrile, take out from an acetonitrile, it was made to dry and sinking-in Ushiro Shigekazu W2 was found. By substituting these values for the following formulas, the degraining particle weight (per sheet unit surface area) of a carbon particle was calculated. The degraining particle weight of a carbon particle (per sheet unit surface area) = (W1-W2) /sheet outside-surface product [0021] (Measuring method of the rate of self-discharge) After charging an electric double layer capacitor in a room temperature and the constant voltage of 2.5V for 12 hours, the circuit was opened, the electric double layer capacitor was left at the room temperature, and it asked for

the rate of self-discharge by the following formulas from Ushiro's voltage change for 72 hours. The rate of self-discharge = 100x (charge voltage -72-hour Ushiro's voltage) / charge voltage

[0022] (Example 1) 80% of powder activated carbon, and carbon black 10%, weighing capacity of the polytetrafluoroethylene (PTFE) 10% was carried out, and it mixed enough with the water of a solid content and this weight, and 50 degrees C of 150-micrometer sheets for polarizable electrodes were fabricated with kneading equipment through this kneading object to the roll-forming machine, after kneading for 10 minutes. The tensile strength of this sheet and the degraining particle weight of a carbon particle were measured, respectively. The result is shown in Table 1.

[0023] It was made to stick to the aluminum foil front face which is a collector 40 by having made the obtained above-mentioned sheet into the polarizable electrode 42, these 2 sets have been arranged so that a polarizable electrode 42 may be made to counter, the propylene-carbonate solution of a 1M4 fluoridation boric acid and 4 ethylammonium which is the electrolytic solution 48 was infiltrated into what inserted the separator 44 made from a cellulose in the meantime, and the electric double layer capacitor was formed in it (refer to drawing 5). Next, the rate of self-discharge of the obtained electric double layer capacitor was measured. The result is shown in Table 1.

[0024] (Example 2) The 80% of the same powder activated carbon as an example 1, and carbon black 10%, weighing capacity of the polytetrafluoroethylene (PTFE) 10% was carried out, and it mixed enough with the water of a solid content and this weight, and 50 degrees C of 150-micrometer sheets were fabricated with kneading equipment through this kneading object to the roll-forming machine, after kneading for 20 minutes. The tensile strength of this sheet and the degraining particle weight of a carbon particle were measured, respectively. The result is shown in Table 1.

[0025] The rate of self-discharge of the electric double layer capacitor which formed the obtained above-mentioned sheet like the example 1, and was obtained in the electric double layer capacitor was measured. The result is shown in Table 1.

[0026] (Example 3) The 85% of the same powder activated carbon as an example 1, and carbon black 10%, weighing capacity of the polytetrafluoroethylene (PTFE) 5% was carried out, and it mixed enough with the water of a solid content and this weight, and 50 degrees C of 150-micrometer sheets were fabricated with kneading equipment through this kneading object to the roll-forming machine, after kneading for 20 minutes. The tensile strength of this sheet and the degraining particle weight of a carbon particle were measured, respectively. The result is shown in Table 1.

[0027] The rate of self-discharge of the electric double layer capacitor which formed the obtained above-mentioned sheet like the example 1, and was obtained in the electric double layer capacitor was measured. The result is shown in Table 1.

[0028] (Example 1 of comparison) After having carried out weighing capacity of the

polytetrafluoroethylene (PTFE) 10%, mixing enough with the water of a solid content and this weight and kneading 50 degrees C with a pressurized kneader for 3 minutes the 80% of the same powder activated carbon as an example 1, and carbon black 10%, drying grinding of this kneading object was carried out. The 150-micrometer sheet was fabricated through this trituration object to the roll-forming machine. The tensile strength of this sheet and the degraining particle weight of a carbon particle were measured, respectively. The result is shown in Table 1.

[0029] The rate of self-discharge of the electric double layer capacitor which formed the obtained above-mentioned sheet like the example 1, and was obtained in the electric double layer capacitor was measured. The result is shown in Table 1.

[0030]

[Table 1]

	引張強さ	脱粒粒子量	自己放電率
実施例1	0.17MPa	0.6mg/cm^2	8%
実施例2	0.24MPa	0.5mg/cm^2	6%
実施例3	0.13MPa	1.0mg/cm^2	9%
比較例1	0.11MPa	1.3mg/cm^2	15%

[0031] (Consideration : examples 1-3, the example 1 of comparison) From the result of Table 1, examples 1-3 were able to make the rate of self-discharge which can set the degraining particle weight of the carbon particle to the inside of the electrolytic solution at the time of real use of two or less 1.0 mg/cm and an electric double layer capacitor 10% or less by setting tensile strength of a polarizable electrode to 0.13 or more MPas.

[0032]

[Effect of the Invention] The polarizable electrode for electric double layer capacitors of this invention can reduce the energy loss by the long-term performance degradation and long-term self-discharge of an electric double layer capacitor by suppressing degraining of the carbon particle in the polarizable electrode at the time of electrolytic-solution sinking in as explained above.

[Brief Description of the Drawings]

[Drawing 1] It is the flow chart which shows an example of the manufacture method of the polarizable electrode of this invention.

[Drawing 2] It is explanatory drawing showing the kneading equipment used by this invention.

[Drawing 3] It is explanatory drawing showing the roll-press equipment used by this invention.

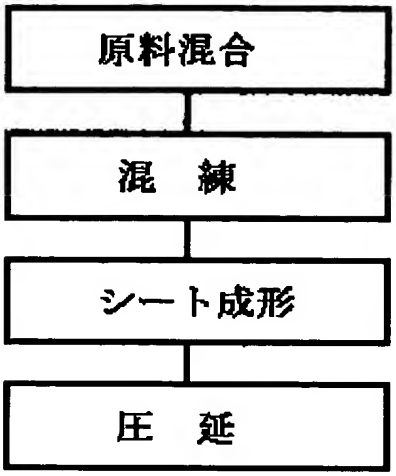
[Drawing 4] It is explanatory drawing showing the rolling equipment (rolling roller) used by this invention.

[Drawing 5] It is the schematic diagram of the electric double layer capacitor in examples 1-3 and the example 1 of comparison.

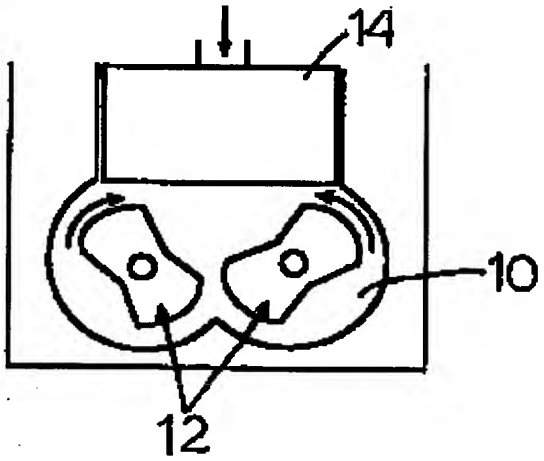
[Description of Notations]

1 [-- A raw material, 4 / -- A sheet-like Plastic solid, 5 / -- The sheet for polarizable electrodes, 10 / -- A kneading tub, 12 / -- A rotor, 14 / -- 20 A kneading lid, 22 / -- 30 The roll for sheet fabrication,, 32 / -- The roll for rolling, 40 / -- A collector, 42 / -- A polarizable electrode, 44 / -- Separator, 46 / -- A case, 48 / -- Electrolytic solution.] -- Mixture, 2 -- A kneading object,

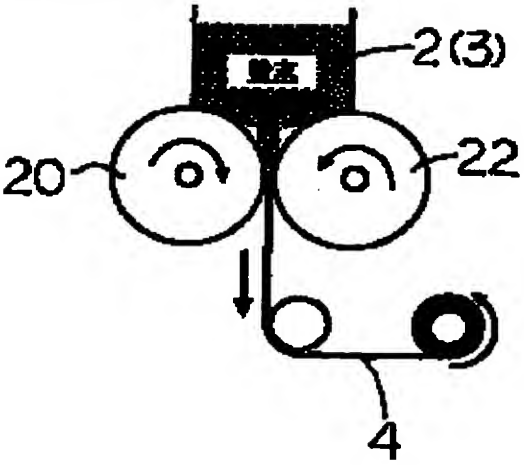
[Drawing 1]



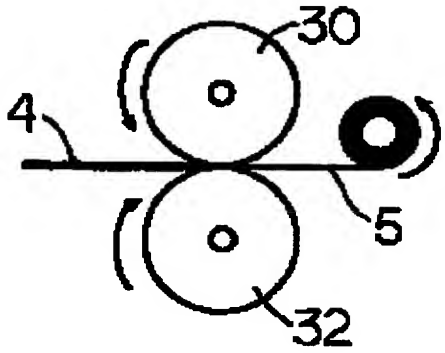
[Drawing 2]



[Drawing 3]



[Drawing 4]



[Drawing 5]